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(72) Inventor TINO VISANI

(54) DEHYDROGENATION OF ZIRCONIUM OR ZIRCONIUM ALLOY BODIES

(71) We, EUROPEAN ATOMIC ENERGY COMMUNITY (EURATOM), of 51—53 Rue Belliard, Brussels, Belgium, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to dehydrogenation of a zirconium or zirconium alloy structure, the surfaces of which are partly in contact with a hydrogenating medium such as water or steam at a high temperature.

More especially the invention relates to structures embodying bodies of zirconium or zirconium alloys such as parts for nuclear reactors, like pressure tubes, which come, when in use, in contact with hydrogenating or corroding media such as hot water or steam. In the case of a pressure tube for a nuclear reactor the part of the tube which comes in contact with hot water or steam may, for example, be the outer surface of the tube, the inner surface of the tube being in contact with a purge gas which contains minor amounts of oxygen or carbon monoxide.

It is known that when zirconium or its alloys are in contact with water or steam under certain conditions, they give rise to corrosion or hydrogenation phenomena in accordance with the following equations:

$$Zr + 2H_2O \rightarrow ZrO_2 + 2H_2 \quad (1)$$

$$Zr + H_2 \rightarrow ZrH_2 \quad (2)$$

Zirconium or its alloys are generally used in nuclear reactors because they have a low neutron capture cross-section and good mechanical properties. The latter are significantly affected by the hydrogen content of the material, owing to the formation of zirconium hydrides which increase the brittleness.

It has now been found, that zirconium and its alloys can be dehydrogenated, so that the hydrogen is extracted from the metal, by covering the part of its surface which is not in contact with the said corroding medium partly or wholly with a metal which catalyzes the reaction of hydrogen with an oxidising medium such as oxygen or carbon monoxide, and by enveloping said part in an atmosphere containing oxygen.

The invention accordingly provides a structure embodying a body of zirconium or of a zirconium alloy having surfaces of which one surface part is exposed to water or steam or other hydrogenating agent and another surface part is exposed to an oxidising agent and having on at least a portion of said another surface part a metallic catalyst for oxidisation by said oxidising agent of hydrogen contained within the zirconium or alloy.

The said catalyst metal, which promotes the reaction between hydrogen in the zirconium metal and an oxydant outside of the zirconium can be any of the metals catalysing or promoting such oxydation-reduction reactions, such as the metals from the group VIII of the Periodic System of the Elements, like rhodium, iridium, palladium, platinum, nickel or iron, or metals such as copper, silver, chromium or cobalt and alloys or mixtures thereof. It has been proved, that these catalyst metals promote the reaction of the hydrogen, even if it is in the form of a solid solution in the zirconium metal or its alloys, with oxygen and/or carbon monoxide at its surface in such a way that the hydrogen is extracted from the whole body of the metal. This reaction between hydrogen and the oxidising gases can also take place at elevated temperatures on condition that an exothermic reaction takes place, that is to say that the so called Gibb's Standard free energy of the reaction. ΔF°, is negative.

The catalyst metal can be applied to the surface of the zirconium metal as a continuous or non-continuous thin layer or coating or it can even be applied to the zirconium

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surface by welding wires or pieces of the catalyst metal on that surface.

For instance, in a nuclear reactor a zirconium or zirconium alloy part, such as a tube, which is on the one side in contact with a hydrogenating medium such as steam at a high temperature, can be covered on the opposite side, which is not in contact with the hydrogenating medium with the thin layer of one or more of the said catalysts, and then on that side an atmosphere is provided, which contains some oxygen or carbon monoxide. This atmosphere can be the gas, used for thermally insulating a pressure tube.

During the process, according to the invention, a continuous diffusion of hydrogen through the zirconium or the zirconium alloys takes place; this hydrogen diffuses through the catalyst and reacts with the oxidizing atmosphere at the catalyst surface.

The thin layers of catalyst metal on the surface of the zirconium or its alloys can be applied thereon by evaporation, sputtering or electro-plating or any other suitable method.

Experiments have been conducted on samples in the form of metal plates (50 × 15 × 0,5 mm) consisting of a zirconium alloy named zircaloy-2, containing hydrogen therein in the form of a solid solution and to which catalyst metal wires were electrically welded on a single surface (i.e. the upper surface) or to which the catalyst metal was applied as a thin coating on one side of the sample. The atmosphere surrounding the samples consisted of argon gas containing 1 vol. % oxygen gas. Some of the results are reported in the following tables:

TABLE 1

Ni-catalyst in the form of wires welded on to one surface of the samples

Sample	Initial hydrogen content (ppm H_2 by weight)	Hydrogen content variation after 20 days (ppm H_2)	Temperature of the sample (°C)
1	279	−111	490
2	268	−76	490
3	262	−74	490

TABLE 2

Ni-catalyst in wire form as in Table 1

Sample	Initial hydrogen content (ppm H_2 by weight)	Hydrogen content variation after 4 days (ppm H_2)	Temperature of the sample (°C)
4	286	−82	520
5	304	−95	520

TABLE 3

Pt-catalyst in form of wires welded on to one surface of the sample

Sample	Initial hydrogen content (ppm H_2 by weight)	Hydrogen content variation after 4 days (ppm H_2)	Temperature of the sample (°C)
7	262	−64	497
8	263	−59	497

TABLE 4

Ni-catalyst in the form of film of a thickness of about 10 μ (sample 9) and of about 5 μ (sample 10)

Sample	Initial hydrogen content (ppm H_2 by weight)	Hydrogen content variation after 2 days (ppm H_2)	Temperature of the sample (°C)
9	280	−83	502
10	306	−104	502

TABLE 5

Ni + noble metal catalyst (about 10 μ Ni + 400 Å Ir on sample 11 and about 5 μ Ni + 400 Å Ir on sample 12).

Sample	Initial hydrogen content (ppm H_2 by (weight)	Hydrogen content variation after 2 days (ppm H_2)	Hydrogen content variation after 3 days (ppm H_2)	Temperature of the sample (°C)
11	297	−148	−215	519
12	306	−162	−186	519

The invention can therefore be used for the non-destructive removal of hydrogen from zirconium metals, especially in nuclear reactors, where these metals are used as mechanical parts, such as nuclear reactor pressure tubes, or fuel element cladding and are in contact with water or steam or with an organic coolant containing traces of water or steam at high temperature.

WHAT WE CLAIM IS:—

1. A structure embodying a body of zirconium or of a zirconium alloy having surfaces of which one surface part is exposed to water or steam or other hydrogenating agent and another surface part is exposed to an oxidising agent and having on at least a portion of said another surface part a metallic catalyst for oxidation by said oxidising agent of hydrogen contained within the zirconium or alloy.

2. A structure as claimed in claim 1 in which the metallic catalyst is in the form of a coating on the zirconium or alloy body.

3. A structure as claimed in claim 1 in which the metallic catalyst is welded to the zirconium or alloy body.

4. A structure as claimed in any one of the preceding claims in which the catalyst is a member of Group VIII of the periodic system of the elements or an alloy or mixture thereof with another metal.

5. A structure as claimed in claim 4 in which the catalyst is or contains nickel.

6. In a nuclear reactor a part composed of zirconium or a zirconium alloy having one side in contact with steam and an opposite side in contact with an atmosphere containing oxygen characterised in that said opposite side is wholly or partly coated with a metallic catalyst for reaction of oxygen and hydrogen or has such a catalyst welded thereto.

BOULT, WADE & TENNANT,
111 and 112, Hatton Garden, London, E.C.1.
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